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(21) International Application Number: PCT/US94/12993 (22) International Filing Date: 10 November 1994 (10.11.94)  (30) Priority Data: 08/150,408           10 November 1993 (10.11.93)   US 08/150,425           10 November 1993 (10.11.93)   US 08/150,426           10 November 1993 (10.11.93)   US  (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).  (72) Inventors: BENNETT, Gregory, S.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). HAAK, Christopher, A.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). GUSTAFSON, Craig, A.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US).  (74) Agents: O'CONNELL, Patrick, J. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).	(81) Designated States: AU, BR, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: PRESSURE SENSITIVE ADHESIVES  (57) Abstract  Pressure sensitive adhesives and tackified pressure sensitive adhesives that are the polymerization product of an acrylic acid ester of a monohydric alcohol whose homopolymer has a $T_g$ less than 0 °C; a non-polar ethylenically unsaturated monomer whose homopolymer has a solubility parameter of no greater than 10.50 and a $T_g$ greater than 15 °C; and 0-5 parts by weight of a polar ethylenically unsaturated monomer whose homopolymer has a solubility parameter of greater than 10.50 and a $T_g$ greater than 15 °C.		

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PRESSURE SENSITIVE ADHESIVESBackground of the InventionField of the Invention

5        This invention relates to pressure sensitive adhesives and tackified pressure sensitive adhesives.

Description of the Background Art

      Acrylate pressure sensitive adhesives are well known in the art. Many of these adhesives are  
10 copolymers of an alkyl ester of acrylic acid and a minor portion of a polar co-monomer. Due to the presence of the polar co-monomer these adhesives generally do not adhere well to low energy and oily surfaces (e.g., surfaces having a critical surface  
15 tension of wetting of no greater than about 35 dynes/cm). Although adhesion can be improved through addition of a tackifier, the degree of improvement is limited because most commercially available tackifiers are not miscible in the polar monomer-containing  
20 adhesive.

Summary of the Invention

      In one aspect, the invention features a pressure sensitive adhesive that includes the polymerization product of:

25        (a) 25-97 parts by weight of an acrylic acid ester of a monohydric alcohol whose homopolymer has a  $T_g$  less than 0°C;

      (b) 3-75 parts by weight of a non-polar ethylenically unsaturated monomer whose homopolymer has  
30 a solubility parameter of no greater than 10.50 and a  $T_g$  greater than 15°C; and

      (c) 0-5 parts by weight of a polar ethylenically unsaturated monomer whose homopolymer has a solubility parameter of greater than 10.50 and a  $T_g$  greater than  
35 15°C. The relative amounts of the acrylic acid ester, the non-polar ethylenically unsaturated monomer, and

the polar ethylenically unsaturated monomer are chosen such that the 90° peel adhesion of the pressure sensitive adhesive to a polypropylene surface is at least 2 lbs/0.5 in. after a 72 hour dwell at room temperature as measured according to Test Procedure B-I, infra.

In second aspect, the invention features a pressure sensitive adhesive that includes the polymerization product of:

10 (a) 25-97 parts by weight of an acrylic acid ester of a monohydric alcohol whose homopolymer has a  $T_g$  less than 0°C;

(b) 3-75 parts by weight of a non-polar ethylenically unsaturated monomer whose homopolymer has a solubility parameter of no greater than 10.50 and a  $T_g$  greater than 15°C; and

(c) 0-5 parts by weight of a polar ethylenically unsaturated monomer whose homopolymer has a solubility parameter of greater than 10.50 and a  $T_g$  greater than 15°C. The relative amounts of the acrylic acid ester, the non-polar ethylenically unsaturated monomer, and the polar ethylenically unsaturated monomer are chosen such that the 90° peel adhesion of the pressure sensitive adhesive to a surface provided with 1.5 ± 0.25 mg/in<sup>2</sup> oil is greater than zero after a 10 second dwell at room temperature as measured according to Test Procedure B-II, infra.

In a third aspect, the invention features a pressure sensitive adhesive that includes:

30 (a) the polymerization product of:

(i) 25-98 parts by weight of an acrylic acid ester of a monohydric alcohol whose homopolymer has a  $T_g$  less than 0°C;

(ii) 2-75 parts by weight of a non-polar ethylenically unsaturated monomer whose homopolymer has

a solubility parameter of no greater than 10.50 and a  $T_g$  greater than 15°C;

(iii) 0-5 parts by weight of a polar ethylenically unsaturated monomer whose homopolymer has  
5 a solubility parameter of greater than 10.50 and a  $T_g$  greater than 15°C; and

(b) at least one tackifier that is miscible in the polymerization product at room temperature.

By "miscible" it is meant that the final pressure  
10 sensitive adhesive does not exhibit macroscopic phase separation as evidenced by optical clarity at room temperature.

In one preferred embodiment, the relative amounts of the acrylic acid ester, non-polar ethylenically  
15 unsaturated monomer, and polar ethylenically unsaturated monomer are chosen such that the 90° peel adhesion of the pressure sensitive adhesive to a polypropylene surface is at least 2 lbs/0.5 in. after a 72 hour dwell at room temperature as measured according  
20 to Test Procedure B1-III, infra.

In another preferred embodiment, the relative amounts of the acrylic acid ester, non-polar ethylenically unsaturated monomer, and polar ethylenically unsaturated monomer are chosen such that  
25 the 90° peel adhesion of the pressure sensitive adhesive to a surface provided with  $1.5 \pm 0.25$  mg/in<sup>2</sup> of oil is greater than zero after a 10 second dwell at room temperature as measured according to Test Procedure B2-III, infra.

30 The solubility parameter referred to herein is calculated according to the technique described in Fedors, Polym. Eng. and Sci., 14:147 (1974). A monomer whose homopolymer has a solubility parameter of greater than 10.50 when measured according to the Fedors  
35 technique is referred to herein as a polar monomer, whereas a monomer whose homopolymer has a solubility

parameter of 10.50 or less when measured according to the Fedors technique is referred to herein as a non-polar monomer.

The invention provides pressure sensitive  
5 adhesives and tackified pressure sensitive adhesives which, by virtue of incorporating a non-polar ethylenically unsaturated monomer and limiting the polar monomer content to no more than 5 parts, exhibit good adhesion to low energy (e.g., plastics such as  
10 polyolefin plastics) surfaces and oily surfaces. The adhesives exhibit good adhesion to high energy surfaces such as stainless steel as well. Because the non-polar monomer reduces the polarity of the adhesive, commercially available tackifiers (many of which have  
15 low polarity themselves) are miscible in the adhesives and thus may be used. Thus, rather than tailoring the tackifier to make it miscible with the acrylate polymer, the invention tailors the properties of the acrylate polymer to make it miscible with the  
20 tackifier.

The adhesives are less toxic than, e.g., adhesives containing polar heteroatom acrylates. The adhesives further exhibit good shear properties both at low and high temperatures, particularly when a small amount (no  
25 more than 5 parts) of a polar co-monomer is included.

The adhesives offer the further advantage of reduced sensitivity to moisture and reduced tendency to corrode metals such as copper relative to pressure sensitive adhesives containing higher amounts of polar  
30 co-monomers. Furthermore, the adhesives interact to a lesser extent with polar additives and, in some cases, increase the solubility of non-polar additives compared to pressure sensitive adhesives containing higher amounts of polar co-monomers.

Other features and advantages of the invention will be apparent from the following description of the preferred embodiments thereof, and from the claims.

Description of the Preferred Embodiments

- 5        One class of pressure sensitive adhesives according to this invention displays good adhesion to both low energy surfaces such as polypropylene and high energy surfaces such as stainless steel. In both cases, the 90° peel strength after a 72 hour dwell is  
10    at least 2 lbs/0.5 in., preferably at least 2.5 lbs/0.5 in., and more preferably at least 3 lbs/0.5 in. measured according to Test Procedure B-I, infra. The adhesives also display good cohesive strength properties as measured by the shear strength.
- 15    Preferably, the shear strength at both room temperature and 70°C is greater than 50 minutes, more preferably greater than 1,000 minutes, and even more preferably greater than 10,000 minutes measured according to Test Procedure C-I, infra.
- 20        A second class of pressure sensitive adhesives according to this invention displays good adhesion to oily surfaces (e.g., oily metal surfaces). Examples of oily surfaces include surfaces provided with mineral oil, emulsion oils, peanut oil, motor oil (e.g., 5W-  
25    30), WD40, and Ferricote 61 A US (Quaker Chemical Co.) (a common protectant for cold rolled steel). The 90° peel adhesion to a surface provided with 1.5 ± 0.25 mg/in<sup>2</sup> oil after a 10 second dwell at room temperature is greater than zero, preferably at least 2 oz./0.5  
30    in., and more preferably at least 4 oz/0.5 in. measured according to Test Procedure B-II, infra. After a 1 minute dwell, the adhesion preferably builds to at least 5 oz/0.5 in. and more preferably to at least 10 oz/0.5 in. measured according to Test Procedure B-II,  
35    infra. The adhesives also display good cohesive strength properties as measured by the shear strength.

Preferably, the shear strength at both room temperature and 70°C is greater than 50 minutes, more preferably greater than 300 minutes, and even more preferably greater than 600 minutes.

5       The tackified pressure sensitive adhesives of this invention display good adhesion to both low energy surfaces such as polypropylene, high energy surfaces such as stainless steel, and oily surfaces (e.g., oily metal). Examples of oily surfaces include surfaces  
10 provided with mineral oil, emulsion oils, peanut oil, motor oil (e.g., 5W-30), WD40, and Ferricote 61 A US (Quaker Chemical Co.) (a common protectant for cold rolled steel).

      The 90° peel adhesion to polypropylene or to steel  
15 after a 72 hour dwell at room temperature is at least 2 lbs/0.5 in., preferably at least 3 lbs/0.5 in., and more preferably at least 4 lbs/0.5 in. measured according to Test Procedure B1-III, infra. The 90° peel adhesion to a surface provided with  $1.5 \pm 0.25$   
20 mg/in<sup>2</sup> of oil after a 10 second dwell at room temperature is greater than zero, preferably at least 2 oz/0.5 in., and more preferably at least 4 oz./0.5 in. measured according to Test Procedure B2-III, infra. After a 1 minute dwell, the adhesion preferably builds  
25 to at least 5 oz/0.5 in. and more preferably to at least 10 oz/0.5 in. measured according to Test Procedure B2-III, infra.

      The tackified adhesives also display good cohesive strength properties as measured by the shear strength.  
30 Preferably, the shear strength at both room temperature and 70°C is greater than 50 minutes, more preferably greater than 1,000 minutes, and even more preferably greater than 10,000 minutes measured according to Test Procedures C1-III and C2-III, infra.

35       The properties of the pressure sensitive adhesives and tackified pressure sensitive adhesives according to



the invention are achieved by controlling the monomeric composition to achieve the appropriate polarity (as measured by the solubility parameter of the homopolymers of the individual monomers determined according to the Fedors technique) and rheological properties ( $T_g$  as measured by the 1 radian/second tan delta maximum temperature of the adhesive polymer).

The ability to incorporate a tackifier increases the value of the peel strength beyond what it would be in the absence of the tackifier. The tackifier also increases "formulation freedom," i.e., the ability to adjust the properties of the adhesives for particular applications by introducing another variable, namely, the tackifier.

A list of several common monomers and their respective Fedors' solubility parameters is shown in Table 1. Table 1 is subdivided into four sections: low  $T_g$  acrylate monomers, high  $T_g$  acrylate monomers, high  $T_g$  methacrylate monomers, and vinyl monomers.

20

TABLE 1: FEDORS' SOLUBILITY PARAMETERS

Repeat Unit		Solubility Parameter (cal/cm <sup>3</sup> ) <sup>0.5</sup>
5	Octadecyl acrylate (ODA)	8.99
	Lauryl acrylate (LA)	9.15
	Iso-octyl acrylate (IOA)	9.22
	2-ethylhexyl acrylate (2-EHA)	9.22
	Butyl acrylate (BA)	9.77
10	Propyl acrylate (PA)	9.95
	Ethyl acrylate (EA)	10.20
15	3,3,5 trimethylcyclohexyl acrylate (TMCA)	9.35
	Iso-bornyl acrylate (IBA)	9.71
	Cyclohexyl acrylate (CHA)	10.16
	N-octyl acrylamide (NOA)	10.33
	Tetrahydrofurfuryl acrylate (THFA)	10.53
20	Methyl acrylate (MA)	10.56
	Glycidyl acrylate (GA)	11.32
	2-Phenoxyethylacrylate (2-PhEA)	11.79
	N-vinylcaprolactam (NVC)	12.10
25	N,N,-Dimethylacrylamide (DMA)	12.32
	N-vinyl-2-pyrrolidone (NVP)	13.38
	Acrylic Acid (AA)	14.04
30		
	Methylmethacrylate (MMA)	9.93
	Ethylmethacrylate (EMA)	9.72
	Propylmethacrylate (PMA)	9.57
	Vinyl Acetate	10.56
	Styrene	11.87

The rheological character of the adhesive polymer can be partially but usefully described by the  $T_g$  as measured by the 1 radian/second tan delta maximum temperature. In the case of adhesives designed for adhesion to low energy surfaces, it is preferable for the  $T_g$  as measured by the 1 radian/second tan delta maximum of the polymer to have a value between  $-45^{\circ}\text{C}$  and  $15^{\circ}\text{C}$ , more preferably between  $-25^{\circ}\text{C}$  and  $0^{\circ}\text{C}$ , and even more preferably between  $-20^{\circ}\text{C}$  and  $-5^{\circ}\text{C}$ . In the case of adhesives designed for adhesion to oily surfaces, it is preferable for the  $T_g$  as measured by the 1 radian/second tan delta maximum temperature of the polymer to have a value between  $-45^{\circ}\text{C}$  and  $15^{\circ}\text{C}$ , more preferably between  $-35^{\circ}\text{C}$  and  $0^{\circ}\text{C}$ , and even more preferably between  $-30^{\circ}\text{C}$  and  $-5^{\circ}\text{C}$ .

In both cases, the adhesives according to the invention having the requisite polarity and rheological properties contain 25-97 parts (more preferably 40-85 parts) of an acrylic acid ester whose homopolymer has a  $T_g$  less than  $0^{\circ}\text{C}$  (more preferably less than  $-20^{\circ}\text{C}$ ), 3-75 parts (more preferably 15-60 parts) of a non-polar ethylenically unsaturated monomer whose homopolymer has a  $T_g$  greater than  $15^{\circ}\text{C}$ , and 0-5 parts (more preferably 0-3 parts) of a polar ethylenically unsaturated monomer whose homopolymer has a  $T_g$  greater than  $15^{\circ}\text{C}$ .

In the case of tackified pressure sensitive adhesives, it is preferable for the 1 radian/second tan delta maximum temperature of the polymer to have a value between  $-45^{\circ}\text{C}$  and  $15^{\circ}\text{C}$ , more preferably between  $-25^{\circ}\text{C}$  and  $5^{\circ}\text{C}$ , and even more preferably between  $-20^{\circ}\text{C}$  and  $0^{\circ}\text{C}$ . The tackified adhesives according to the invention having the requisite polarity and rheological properties contain 25-98 parts (more preferably 70-97 parts) of an acrylic acid ester whose homopolymer has a  $T_g$  less than  $0^{\circ}\text{C}$  (more preferably less than  $-20^{\circ}\text{C}$ ), 2-75 parts (more preferably 3-30 parts) of a non-polar

ethylenically unsaturated monomer whose homopolymer has a  $T_g$  greater than  $15^\circ\text{C}$ , 0-5 parts (more preferably 0-3 parts) of a polar ethylenically unsaturated monomer whose homopolymer has a  $T_g$  greater than  $15^\circ\text{C}$ , and one or 5 more tackifiers.

In all cases, the acrylic acid ester is a monofunctional acrylic ester of a monohydric alcohol having from about 4 to about 18 carbon atoms in the alcohol moiety whose homopolymer has a  $T_g$  less than  $0^\circ\text{C}$ . 10 Included in this class of acrylic acid esters are isooctyl acrylate, 2-ethylhexyl acrylate, isononyl acrylate, isodecyl acrylate, decyl acrylate, lauryl acrylate, hexyl acrylate, butyl acrylate, and octadecyl acrylate, or combinations thereof. In the case of 15 octadecyl acrylate, the amount is chosen such that side chain crystallization does not occur at room temperature.

The non-polar ethylenically-unsaturated monomer is a monomer whose homopolymer has a solubility parameter 20 as measured by the Fedors method of not greater than 10.50 and a  $T_g$  greater than  $15^\circ\text{C}$ . The non-polar nature of this monomer improves the low energy surface adhesion and oily surface adhesion of the adhesive. It also improves the structural properties of the adhesive 25 (e.g., cohesive strength) relative to a homopolymer of the acrylic acid ester described above. Examples of suitable non-polar monomers include 3,3,5 trimethylcyclohexyl acrylate, cyclohexyl acrylate, isobornyl acrylate, N-octyl acrylamide, t-butyl 30 acrylate, methyl methacrylate, ethyl methacrylate, and propyl methacrylate or combinations thereof.

The adhesive may contain a limited quantity (e.g., no more than 5 parts) of a polar ethylenically unsaturated monomer whose homopolymer has a solubility 35 parameter as measured by the Fedors method of greater than 10.50 and a  $T_g$  greater than  $15^\circ\text{C}$  to improve

structural properties (e.g., cohesive strength). It is not desirable to include more than 5 parts of the polar monomer because the polar monomer impairs low energy surface adhesion and oily surface adhesion, and reduces tackifier miscibility. Examples of suitable polar monomers include acrylic acid, itaconic acid, certain substituted acrylamides such as N,N dimethylacrylamide, N-vinyl-2-pyrrolidone, N-vinyl caprolactam, acrylonitrile, tetrahydrofurfuryl acrylate, glycidyl acrylate, 2-phenoxyethylacrylate, and benzylacrylate, or combinations thereof.

In the case of tackified compositions, the tackifier must be miscible with the acrylate-containing polymer of the adhesive such that macroscopic phase separation does not occur in order to improve the properties of the adhesive. Preferably, the adhesive is free of microscopic phase separation as well. Most commercially available tackifiers are hydrocarbon-based and thus of low polarity. Such tackifiers ordinarily are not miscible with conventional, polar monomer-containing adhesives. However, by incorporating a non-polar monomer into the adhesive (thereby increasing the non-polar character of the adhesive) the invention allows a variety of commercially available tackifiers to be used. The total amount of tackifier is preferably 5-60 parts per 100 parts acrylate-containing polymer, and more preferably about 15-30 parts. The particular amount of tackifier depends on the composition of the acrylate-containing polymer and is generally selected to maximum peel properties without compromising desired shear strength.

Because the adhesives are preferably prepared by polymerizing the monomers in the presence of the tackifier according to a free radical process, it is further desirable to select a tackifier that does not substantially impede the polymerization process, e.g.,

by acting as a free radical scavenger, chain termination agent, or chain transfer agent. A measure of the ability of the tackifier to inhibit free radical polymerization in a bulk polymerization process for a given process condition is defined here as the "inhibition factor." The inhibition factor (IF) is determined from the monomer conversion test and is the ratio of (1) the percent volatiles of the tackified sample ( $C_t$ ) less the percent volatiles of an identically formulated and processed sample without tackifier ( $C_o$ ) and (2) the percent volatiles of an identically formulated and processed sample without tackifier ( $C_o$ ). The inhibition factor equation is shown below:

$$\text{IF} = \frac{(C_t - C_o)}{C_o}$$

Although a wide variety of tackifiers may be used, in cases where free radical polymerization is involved the class of tackifiers known under the tradename Regalrez resins commercially available from Hercules are preferred. These tackifiers are produced by polymerization and hydrogenation of pure monomer hydrocarbon feed stock. Suitable resins include Regalrez resins 1085, 1094, 6108, and 3102.

The monomer mixture can be polymerized by various techniques, with photoinitiated bulk polymerization being preferred. An initiator is preferably added to aid in polymerization of the monomers. The type of initiator used depends on the polymerization process. Photoinitiators which are useful for polymerizing the acrylate monomers include benzoin ethers such as benzoin methyl ether or benzoin isopropyl ether, substituted benzoin ethers such as 2-methyl-2-hydroxylpropiophenone, aromatic sulfonyl chlorides such as 2-naphthalenesulfonyl chloride, and photoactive

oxides such as 1-phenyl-1,2-propanedione-2-(o-ethoxycarbonyl)oxime. An example of a commercially available photoinitiator is Irgacure<sup>TM</sup> 651 available from Ciba-Geigy Corporation, having the formula 2,2-dimethoxy-1,2-diphenylethane-1-one). Generally, the photoinitiator is present in an amount of about 0.005 to 1 weight percent based on the weight of the monomers. Examples of suitable thermal initiators include AIBN and peroxides.

- 10       The mixture of the polymerizable monomers may also contain a crosslinking agent, or a combination of crosslinking agents, to increase the shear strength of the adhesive. Useful crosslinking agents include substituted triazines such as 2,4,-
- 15 bis(trichloromethyl)-6-(4-methoxy phenyl)-s-triazine, 2,4-bis(trichloromethyl)-6-(3,4-dimethoxyphenyl)-s-triazine, and the chromophore-substituted halo-s-triazines disclosed in U.S. Patent Nos. 4,329,384 and 4,330,590 (Vesley) incorporated herein by reference.
- 20 Other useful crosslinking agents include multifunctional alkyl acrylate monomers such as trimetholpropane triacrylate, pentaerythritol tetra-acrylate, 1,2 ethylene glycol diacrylate, 1,4 butanediol diacrylate, 1,6 hexanediol diacrylate, and
- 25 1,12 dodecanol diacrylate. Various other crosslinking agents with different molecular weights between (meth)acrylate functionality would also be useful. Generally, the crosslinker is present in an amount of about 0.005 to 1 weight percent based on the combined
- 30 weight of the monomers.

Where a foam-like pressure sensitive adhesive tape is desired, a monomer blend containing microspheres may be used. Suitable microspheres are commercially available from Kema Nord Plastics under the trade name

35 "Expancel" and from Matsumoto Yushi Seiyaku under the trade name "Micropearl". When expanded the

microspheres have a specific density of approximately 0.02-0.036 g/cc. It is possible to include the unexpanded microspheres in the pressure sensitive adhesive composition and subsequently heat them to  
5 cause expansion when they are appropriately processed, but it is generally preferred to mix the expanded microspheres into the adhesive. This process makes it easier to ensure that the hollow microspheres in the final adhesive are substantially surrounded by at least  
10 a thin layer of adhesive.

Polymeric microspheres having an average diameter of 10 to 200 micrometers may be blended into the polymerizable composition in amounts from about 15% to about 75% by volume prior to coating. Also useful are  
15 glass microspheres having an average diameter of from 5 to 200 micrometers, preferably from about 20 to 80 micrometers. Such microspheres may comprise 5% to 65% by volume of the pressure sensitive adhesive. Both polymeric and glass microspheres are known in the art.  
20 The pressure sensitive adhesive layer of the tape should be at least 3 times as thick as the diameter of the microspheres, preferably at least 7 times.

Other tape constructions in which the pressure sensitive adhesives according to the invention are  
25 useful include mechanical fasteners such as Dual-Lock<sup>TM</sup> brand fastener (Minnesota Mining and Manufacturing Co., St. Paul, MN) and Scotchmate<sup>TM</sup> brand fastener (Minnesota Mining and Manufacturing Co., St. Paul, MN). The pressure sensitive adhesives are also useful in  
30 vibration damping applications.

Other materials which can be blended with the polymerizable monomers prior to coating include plasticizers, tackifiers, coloring agents, reinforcing agents, fire retardants, foaming agents, thermally  
35 conductive agents, electrically conductive agents,



post-curing agents, and post-curing agent curatives and their accelerators, and the like.

The pressure sensitive adhesives according to the invention are preferably prepared by photoinitiated bulk polymerization according to the technique described in Martens et al., U.S. Patent no. 4,181,752. The polymerizable monomers and a photoinitiator are mixed together in the absence of solvent and partially polymerized to a viscosity in the range of from about 500 cps to about 50,000 cps to achieve a coatable syrup. Alternatively, the monomers may be mixed with a thixotropic agent such as fumed hydrophilic silica to achieve a coatable thickness. The crosslinking agent and any other ingredients (including any tackifiers) are then added to the prepolymerized syrup. Alternatively, these ingredients (including any tackifiers but with the exception of the crosslinking agent) can be added directly to the monomer mixture prior to pre-polymerization.

The resulting composition is coated onto a substrate (which may be transparent to ultraviolet radiation) and polymerized in an inert (i.e., oxygen free) atmosphere, e.g., a nitrogen atmosphere by exposure to ultraviolet radiation. Examples of suitable substrates include release liners (e.g., silicone release liners) and tape backings (which may be primed or unprimed paper or plastic). A sufficiently inert atmosphere can also be achieved by covering a layer of the polymerizable coating with a plastic film which is substantially transparent to ultraviolet radiation, and irradiating through that film in air as described in the aforementioned Martens et al. patent using ultraviolet lamps. Alternatively, instead of covering the polymerizable coating, an oxidizable tin compound may be added to the polymerizable syrup to increase the tolerance of the

syrup to oxygen as described in U.S. Pat. No. 4,303,485 (Levens). The ultraviolet light source preferably has 90% of the emissions between 280 and 400 nm (more preferably between 300 and 400 nm), with a maximum at 5 351 nm.

Tackifiers may also be added after polymerization of the acrylate monomers.

Where multi-layer tape constructions are desirable, one method of construction is multi-layer coating using conventional techniques. For example, 10 the coatings may be applied concurrently (e.g., through a die coater), after which the entire multi-layer structure is cured all at once. The coatings may also be applied sequentially whereby each individual layer 15 is partially or completely cured prior to application of the next layer.

The invention will now be further described by way of the following examples.

#### EXAMPLES

##### 20 I. Adhesives for Low Energy Surfaces

##### Test Procedures-Low Energy Surface Adhesion

Test procedures used in the examples to evaluate pressure sensitive adhesives useful for adhesion to low energy surfaces include the following.

##### 25 Monomer Conversion Test (Test Procedure A-I)

The monomer conversion was determined gravimetrically. A sample of the adhesive was weighed after it was coated and subsequently dried at 120°C for 3 hours and then re-weighed. The percent volatiles was 30 taken to be indicative of the monomer conversion.

##### 90° Peel Adhesion Test (Test Procedure B-I)

One-half inch wide strips of the adhesive sample were carefully cut and placed onto the substrate of interest. The adhesive thickness was 5 mils. A 5 mil 35 anodized aluminum backing (0.625 in, wide) was then laminated to the adhesive which is approximately 5

inches long. Test substrates of interest included low energy surfaces such as polypropylene (2" x 5" x 3/16" natural polypropylene panels from Precision Punch and Plastic, Minneapolis, MN, with a mask on both sides  
5 that is removed prior to cleaning and testing) and polycarbonate (Lexan<sup>TM</sup> from General Electric Co.), and high energy surfaces such as stainless steel (304-2BA 28 gauge stainless steel with a surface roughness of  $2.0 \pm 1.0$  microinches). A free end of the backing to  
10 which the adhesive was laminated extended beyond the test substrate so that it could be clamped to a load cell to determine peel strength.

The sample was rolled back and forth twice with a 2 kg hard rubber roller to ensure contact between the  
15 adhesive and the test substrate. The adhesive was then removed after a given dwell time (usually 72 hours unless otherwise noted) at 12"/minute in a 90° peel mode.

The stainless steel substrates were washed once  
20 with acetone and 3 times with a 50/50 isopropanol/water mixture prior to testing. The plastic substrates were washed 3 times with heptane prior to testing. The results are reported in lbs/0.5 in. width as the average of 2 tests. All tests were conducted at room  
25 temperature.

#### Shear Test (Test Procedure C-I)

A 0.5 inch strip of tape was adhered to a piece of stainless steel (304-2BA 28 gauge stainless steel with a surface roughness of  $2.0 \pm 1.0$  microinches) which had  
30 been cleaned once with acetone and 3 times with 50/50 isopropanol/water such that a one-half square inch overlap was accomplished. A piece of 5 mil anodized aluminum (0.625 in. wide) was then laminated to the entire area of the pressure sensitive adhesive, leaving  
35 an additional area to which a load could be applied. The adhesive thickness was 5 mils. The sample was then

rolled back and forth twice with a 15 pound roller and allowed to dwell for four hours. The 70°C samples were allowed to dwell for an additional 10 minutes. After dwelling the sample was tested at either room temperature or 70°C. At room temperature a 1 kg load was applied to the adhesive and the time before the load fell was recorded. At 70°C a 500g load was applied to the adhesive and the time before the load fell was recorded. The results are reported as the average of 2 tests.

#### Comparative Examples-Low Energy Surface Adhesion

##### Comparative Example C1

A premix was prepared using 90 parts isooctyl acrylate (IOA), 10 parts acrylic acid (AA), and 0.04 parts 2,2-dimethoxy-2-phenylacetophenone photoinitiator (Irgacure TM 651, available from Ciba Geigy Corp.) This mixture was partially polymerized under a nitrogen-rich atmosphere by exposure to ultraviolet radiation to provide a coatable syrup having a viscosity of about 3000 cps. 0.15 parts of 2,6-bis-trichloromethyl-6-(4-methoxyphenyl)-s-triazine and an additional 0.16 parts of Irgacure<sup>TM</sup> 651 were added to the syrup and it was then knife coated onto a silicone-treated polyethylene-coated paper release liner at a thickness of 5 mils. The resulting composite was then exposed to ultraviolet radiation having a spectral output from 300-400 nm with at maximum at 351 nm in a nitrogen-rich environment. An intensity of about 1.0 mW/cm<sup>2</sup> was used for the first one-third of the exposure time and an intensity of about 2.2 mW/cm<sup>2</sup> was used for the second two-thirds of exposure time, resulting in a total energy of 250 mJ/cm<sup>2</sup>. The adhesive was then tested according to the test methods listed above and the results are shown in Table I-2. The designation "RT" means room temperature.

### Comparative Examples C2 and C3

Comparative example C2 was prepared in the same way as comparative example C1 except that a premix of 94 parts of IOA and 6 parts of AA was used.

- 5 Comparative example C3 was prepared in the same way as comparative example C1 except that a premix of 100 parts of IOA and 0 parts of AA was used. Comparative examples C2 and C3 were tested according to the test methods listed above and the results are shown in Table I-2.
- 10 I-2.

TABLE I-2

Ex.	Stainless Steel Peel Strength	Poly-propylene Peel Strength	R.T. Shear (Minutes)	70° Shear (minutes)	Percent Conversion
C1	5.33	0.43	10,000+	10,000+	>98.5%
C2	3.73	1.29	10,000+	10,000+	>98.5%
15 C3	1.35	1.53	2	3	>98.5%

### Examples-Low Energy Surface Adhesion

#### Examples 1-23

- 20 Example 1 was prepared in the same way as comparative example C1 except the premix consisted of 66 parts IOA, 33.5 parts isobornyl acrylate (IBA), and 0.5 parts of AA. In addition, 0.09 parts of 2,6-bis-trichloromethyl-6-(4-methoxyphenyl)-s-triazine were
- 25 added after the premix was partially polymerized. The composite was exposed to ultraviolet radiation having a spectral output from 300-400 nm with at maximum at 351 nm in a nitrogen-rich environment at an average intensity of about 2.05 mW/cm<sup>2</sup>. The total energy was
- 30 650 mJ/cm<sup>2</sup>.

Example 2 was prepared in the same way as Example 1 except a premix consisting of 69 parts IOA, 30 parts IBA, and 1 part AA was used.

Example 3 was prepared in the same way Example 1 except a premix consisting of 65.5 parts IOA, 34.25 parts IBA, and 0.25 parts AA was used.

Example 4 was prepared in the same way as Example 1 except a premix consisting of 65 parts IOA and 35 parts IBA was used and 0.05 parts of 2,5-bis-trichloromethyl-6-(4-methoxyphenyl)-s-triazine was used.

Example 5 was prepared in the same way as Example 4 except a premix of 55 parts IOA and 45 parts (3,3,5-trimethylcyclohexyl acrylate (TMCA) was used.

Example 6 was prepared in the same way as Example 5 except 0.10 parts of 2,6-bis-trichloromethyl-4-(p-methoxyphenyl)-s-triazine was used.

Example 7 was prepared in the same way as Example 1 except a premix of 72 parts of IOA, 27 parts of IBA, and 1 part of AA was used.

Example 8 was prepared in the same way as Example 1 except a premix of 66 parts of IOA, 33 parts of IBA, and 1 part of AA was used.

Example 9 was prepared in the same way as Example 1 except a premix of 63 parts of IOA, 36 parts of IBA, and 1 part of AA was used.

Example 10 was prepared in the same way as Example 1 except a premix of 70.75 parts of IOA, 29 parts of TMCA, and 0.25 parts of AA was used.

Example 11 was prepared in the same way as Example 1 except a premix of 64.5 parts of IOA, 35 parts of TMCA, and 0.5 parts of AA was used.

Example 12 was prepared in the same way as Example 1 except a premix of 49 parts of IOA, 51.5 parts of cyclohexyl acrylate (CHA), and 0.5 parts of AA was used.

Example 13 was prepared in the same way as Example 1 except a premix of 80 parts of IOA, 19.5 parts of N-octylacrylamide (NOA), and 0.5 parts of AA was used.

Example 14 was prepared in the same way as Example 6 except a premix of 90 parts IOA, 10 parts IBA, and 0.5 parts AA was used.

Example 15 was prepared in the same way as Example 6 except a premix of 80 parts IOA, 20 parts IBA, and 0.5 parts AA was used.

Example 16 was prepared in the same way as Example 6 except a premix of 70 parts IOA, 30 parts IBA, and 0.5 parts AA was used.

Example 17 was prepared in the same way as Example 6 except a premix of 90 parts IOA, 10 parts TMCA, and 0.5 parts AA was used.

Example 18 was prepared in the same way as Example 6 except a premix of 80 parts IOA, 20 parts TMCA, and 0.5 parts AA was used.

Example 19 was prepared in the same way as Example 6 except a premix of 70 parts IOA, 30 parts TMCA, and 0.5 parts AA was used.

Example 20 was prepared in the same way as Example 6 except a premix of 60 parts IOA, 40 parts TMCA, and 0.5 parts AA was used.

Example 21 was prepared in the same way as Example 6 except a premix of 55 parts IOA, 45 parts TMCA, and 0.5 parts AA was used.

Example 22 was prepared in the same way as Example 6 except a premix of 50 parts IOA, 50 parts CHA, and 0.5 parts AA was used.

Example 23 was prepared in the same way as Example 6 except a premix of 45 parts IOA, 55 parts CHA, and 0.5 parts AA was used.

The data of Examples 1-23 are shown in Table I-3. In the table "St. St." refers to stainless steel. The designation "n.t." means not tested. The designation "RT" means room temperature. The designation "(1/2)" means that 1 of the 2 samples tested passed the test. The samples for peel testing in Examples 4 and 5 were

prepared using a 15 lb roller. A 24 hr. dwell period was used. Because Examples 13, 14, 17, 18, 22, and 23 do not meet the minimum peel adhesion requirement, they are included here as further comparative examples.

5

TABLE I-3

	Ex.	St.St.	Polyprop.	Polycarb.	RT Shear	70°C Shear	% Conv.
10	1	3.10	3.11	4.93	10K+	10K+	>98.5%
	2	3.34	2.62	4.29	10K+	10K+	>98.5%
	3	3.41	3.35	4.39	10K+	10K+	>98.5%
	4	3.50	2.80	4.81	1409	51	>98.5%
	5	3.08	2.74	nt	2960	143	>98.5%
15	6	3.22	2.45	4.20	1138	324	>98.5%
	7	3.28	2.48	nt	10K+	10K+	>98.5%
	8	3.21	2.04	nt	10K+	10K+	>98.5%
	9	3.14	2.12	nt	10K+	10K+	>98.5%
	10	3.18	2.43	nt	3375	10K+	>98.5%
20	11	2.39	2.08	2.92	10K+	10K+	>98.5%
	12	3.56	2.52	3.68	3960	10K+	>98.5%
	13	2.10	1.71	2.61	2334	10K+	>98.5%
	14	1.49	1.57	nt	1207	10K+ (1/2)	>98.5%
	15	1.84	1.85	nt	3133	10K+	>98.5%
25	16	2.23	2.28	nt	10K+ (1/2)	2058	>98.5%
	17	1.65	1.87	nt	1103	10K+	>98.5%
	18	1.65	1.89	nt	3747	10K+	>98.5%
	19	1.89	2.16	nt	10K+ (1/2)	10K+	>98.5%
	20	2.31	2.41	nt	10K+	10K+	>98.5%
30	21	1.90	2.69	nt	10K+	10K+	>98.5%
	22	2.87	1.18	nt	10K+	10K+	>98.5%
	23	3.53	0.95	nt	10K+	10K+	>98.5%

The data of Table I-3 shows that the adhesion to low energy surfaces like polypropylene can be increased without decreasing the adhesion to high energy surface



such as stainless steel as was observed in the comparative examples of Table I-2. In addition the data of Table I-3 shows that desirable cohesive strength properties can also be achieved in the  
5 pressure sensitive adhesives of this invention.

## II. Adhesives for Oily Surface Adhesion

### Test Procedures-Oily Surface Adhesion

Test procedures used in the examples to evaluate  
10 pressure sensitive adhesives useful for adhesion to oily surfaces include the following.

#### Monomer Conversion Test (Test Procedure A-II)

The monomer conversion was determined gravimetrically. 3 in. by 3 in. samples were laminated  
15 to a piece of aluminum foil, weighed, and placed in a forced air oven at 250°F for 90 min. Samples were then equilibrated at room temperature and reweighed for weight loss. The percent volatiles was taken to be indicative of the monomer conversion.

#### 20 90° Peel Adhesion Test (Test Procedure B-II)

One-half inch wide pieces of samples were cut out and laminated to 5 mil thick anodized aluminum which was 0.625 in. wide. The adhesive thickness was 5 mils. The release liner was then removed from the adhesive  
25 and the samples were placed onto either a stainless steel substrate (304 stainless steel with a #7 finish) or a cold rolled steel substrate (20 gauge cold plate CRS 1018 with mill finish). The stainless steel substrate was cleaned prior to application of adhesive  
30 by wiping once with acetone and 3 times with heptane. The cold rolled steel substrate was cleaned prior to application of adhesive by wiping once with acetone.

Prior to application of the adhesive, an excess of mineral oil was applied to each cold rolled steel  
35 substrate with a small piece of cheese cloth and then removed to leave a coating of oil that was  $1.5 \pm 0.25$

prepared using a 15 lb roller. A 24 hr. dwell period was used. Because Examples 13, 14, 17, 18, 22, and 23 do not meet the minimum peel adhesion requirement, they are included here as further comparative examples.

5

TABLE I-3

	Ex.	St.St.	Polyprop.	Polycarb.	RT Shear	70°C Shear	% Conv.
10	1	3.10	3.11	4.93	10K+	10K+	>98.5%
	2	3.34	2.62	4.29	10K+	10K+	>98.5%
	3	3.41	3.35	4.39	10K+	10K+	>98.5%
	4	3.50	2.80	4.81	1409	51	>98.5%
	5	3.08	2.74	nt	2960	143	>98.5%
15	6	3.22	2.45	4.20	1138	324	>98.5%
	7	3.28	2.48	nt	10K+	10K+	>98.5%
	8	3.21	2.04	nt	10K+	10K+	>98.5%
	9	3.14	2.12	nt	10K+	10K+	>98.5%
	10	3.18	2.43	nt	3375	10K+	>98.5%
20	11	2.39	2.08	2.92	10K+	10K+	>98.5%
	12	3.56	2.52	3.68	3960	10K+	>98.5%
	13	2.10	1.71	2.61	2334	10K+	>98.5%
	14	1.49	1.57	nt	1207	10K+ (1/2)	>98.5%
	15	1.84	1.85	nt	3133	10K+	>98.5%
25	16	2.23	2.28	nt	10K+ (1/2)	2058	>98.5%
	17	1.65	1.87	nt	1103	10K+	>98.5%
	18	1.65	1.89	nt	3747	10K+	>98.5%
	19	1.89	2.16	nt	10K+ (1/2)	10K+	>98.5%
	20	2.31	2.41	nt	10K+	10K+	>98.5%
30	21	1.90	2.69	nt	10K+	10K+	>98.5%
	22	2.87	1.18	nt	10K+	10K+	>98.5%
	23	3.53	0.95	nt	10K+	10K+	>98.5%

The data of Table I-3 shows that the adhesion to low energy surfaces like polypropylene can be increased without decreasing the adhesion to high energy surface

such as stainless steel as was observed in the comparative examples of Table I-2. In addition the data of Table I-3 shows that desirable cohesive strength properties can also be achieved in the pressure sensitive adhesives of this invention.

## II. Adhesives for Oily Surface Adhesion

### Test Procedures-Oily Surface Adhesion

Test procedures used in the examples to evaluate pressure sensitive adhesives useful for adhesion to oily surfaces include the following.

#### Monomer Conversion Test (Test Procedure A-II)

The monomer conversion was determined gravimetrically. 3 in. by 3 in. samples were laminated to a piece of aluminum foil, weighed, and placed in a forced air oven at 250°F for 90 min. Samples were then equilibrated at room temperature and reweighed for weight loss. The percent volatiles was taken to be indicative of the monomer conversion.

#### 90° Peel Adhesion Test (Test Procedure B-II)

One-half inch wide pieces of samples were cut out and laminated to 5 mil thick anodized aluminum which was 0.625 in. wide. The adhesive thickness was 5 mils. The release liner was then removed from the adhesive and the samples were placed onto either a stainless steel substrate (304 stainless steel with a #7 finish) or a cold rolled steel substrate (20 gauge cold plate CRS 1018 with mill finish). The stainless steel substrate was cleaned prior to application of adhesive by wiping once with acetone and 3 times with heptane. The cold rolled steel substrate was cleaned prior to application of adhesive by wiping once with acetone.

Prior to application of the adhesive, an excess of mineral oil was applied to each cold rolled steel substrate with a small piece of cheese cloth and then removed to leave a coating of oil that was  $1.5 \pm 0.25$

mg/in.<sup>2</sup>. A free end of the backing to which the adhesive was laminated extended beyond the test substrate so that it could be clamped to a load cell to determine peel strength. The sample was rolled back and forth twice with a 4.5 lb roller to ensure contact between the adhesive and the test substrate. The adhesive was then removed after a given dwell time (10 sec., 1 minute, or 24 hours) at 12"/minute in a 90° peel mode.

10 The values reported are in oz/0.5 in. and represent the average peel values (based on two tests) obtained between 1 and 4 inches on a 5 inch peel sample. All tests were done at room temperature.

Shear Test (Test Procedure C-II)

15 One-half inch wide pieces of samples were cut out and laminated to 5 mil thick anodized aluminum which was 0.625 in. wide. This construction was placed on stainless steel panels (304 stainless steel with a #7 finish) that had been cleaned by wiping once with acetone and 3 times with heptane. Placement was such that a 1.0 in. x 0.5 in. adhesive sample (adhesive thickness = 5 mils) was in contact with the panel. The adhesive sample was rolled back and forth twice with a 4.5 lb roller, with some excess material overhanging the sample for attachment of the weight. The samples were then allowed to dwell for 24 hours before the weight was hung on the samples. The 70°C samples were further allowed to dwell for an additional 10 minutes in the oven before the weight was applied. For the room temperature samples, a 1000 g weight was used, whereas for the 70°C samples a 500 g weight was used.

The shear data are reported in minutes until the weight fell and represent the average of two tests.

Phase Separation (Test Procedure D-II)

35 The presence or absence of phase separation was judged by the optical clarity of the resulting

### Comparative Examples-Oily Surface Adhesion

## 5

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### Comparative Examples C2 and C3

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### Examples-Oily Surface Adhesion

### Examples 1-20

3

acrylate (LA). The NDA was heated to about 40°C prior to syruping and coating. In addition, 0.08 parts of 2,4-bis-trichloromethyl-6-(3,4-dimethoxyphenyl)-s-triazine were added after the premix was partially  
5 polymerized.

Example 2 was prepared in the same way as example 1 except that the premix consisted of 35 parts NOA and 65 parts LA. The NOA was heated to about 40°C prior to syruping and coating. In addition, 0.12 parts of 2,4-  
10 bis-trichloromethyl-6-(3,4-dimethoxyphenyl)-s-triazine were added after the premix was partially polymerized.

Example 3 was prepared in the same way as example 1 except that the premix consisted of 45 parts NOA and 55 parts LA. The NOA was heated to about 40°C prior to  
15 syruping and coating.

Example 4 was prepared in the same way as example 1 except that the premix consisted of 25 parts isobornyl acrylate (IBA) and 75 parts IOA.

Example 5 was prepared in the same way as example  
20 1 except that the premix consisted of 30 parts IBA and 70 parts LA.

Example 6 was prepared in the same way as example 1 except that the premix consisted of 40 parts IBA and 60 parts LA. In addition, 0.12 parts of 2,6-bis-  
25 trichloromethyl-6-(3,4-dimethoxyphenyl)-s-triazine were added after the premix was partially polymerized.

Example 7 was prepared in the same way as example 1 except that the premix consisted of 30 parts IBA and 70 parts iso-decyl acrylate (IDA).

30 Example 8 was prepared in the same way as example 1 except that the premix consisted of 40 parts IBA and 60 parts IDA. In addition, 0.12 parts of 2,4-bis-trichloromethyl-6-(3,4-dimethoxyphenyl)-s-triazine were added after the premix was partially polymerized.

35 Example 9 was prepared in the same way as example 1 except that the premix consisted of 40 parts IBA, 15

parts IOA, and 45 parts LA. In addition, 0.12 parts of 2,4-bis-trichloromethyl-6-(3,4-dimethoxyphenyl)-s-triazine were added after the premix was partially polymerized.

5        Example 10 was prepared in the same way as example 1 except that the premix consisted of 35 parts NOA, 15 parts IOA, and 50 parts LA. The NOA was heated to about 40°C prior to syringing and coating. In addition, 0.12 parts of 2,4-bis-trichloromethyl-6-(3,4-  
10 dimethoxyphenyl)-s-triazine were added after the premix was partially polymerized.

      Example 11 was prepared in the same way as example 1 except that the premix consisted of 35 parts NOA, 35 parts IOA, and 30 parts LA. The NOA was heated to  
15 about 40°C prior to syringing and coating. In addition, 0.12 parts of 2,4-bis-trichloromethyl-6-(3,4-dimethoxyphenyl)-s-triazine were added after the premix was partially polymerized.

      Example 12 was prepared in the same way as example  
20 1 except that the premix consisted of 35 parts NOA, 45 parts IOA, and 20 parts LA. The NOA was heated to about 40°C prior to syringing and coating. In addition, 0.12 parts of 2,4-bis-trichloromethyl-6-(3,4-dimethoxyphenyl)-s-triazine were added after the premix  
25 was partially polymerized.

      Example 13 was prepared in the same way as example 1 except that the premix consisted of 35 parts IBA, 15 parts IOA, and 50 parts octadecyl acrylate (ODA). In addition, 0.12 parts of 2,4-bis-trichloromethyl-6-(3,4-  
30 dimethoxyphenyl)-s-triazine were added after the premix was partially polymerized.

      Example 14 was prepared in the same way as example 1 except that the premix consisted of 35 parts IBA, 35 parts IOA, and 30 parts ODA. In addition, 0.12 parts  
35 of 2,4-bis-trichloromethyl-6-(3,4-dimethoxyphenyl)-s-

triazine were added after the premix was partially polymerized.

Example 15 was prepared in the same way as example 1 except that the premix consisted of 35 parts IBA, 45 parts IOA, and 20 parts ODA. In addition, 0.12 parts of 2,4-bis-trichloromethyl-6-(3,4-dimethoxyphenyl)-s-triazine were added after the premix was partially polymerized.

Example 16 was prepared in the same way as example 1 except that the premix consisted of 30 parts NOA, 40 parts IOA, and 30 parts ODA. The NOA was heated to about 40°C prior to syringing and coating. In addition, 0.12 parts of 2,4-bis-trichloromethyl-6-(3,4-dimethoxyphenyl)-s-triazine were added after the premix was partially polymerized.

Example 17 was prepared in the same way as example 1 except that the premix consisted of 67 parts IOA, 32.5 parts IBA, and 0.5 parts AA. In addition, 0.12 parts of 2,4-bis-trichloromethyl-6-(3,4-dimethoxyphenyl)-s-triazine were added after the premix was partially polymerized.

Example 18 was prepared in the same way as example 1 except that the premix consisted of 69 parts IOA, 30 parts IBA, and 1 part AA. In addition, 0.12 parts of 2,4-bis-trichloromethyl-6-(3,4-dimethoxyphenyl)-s-triazine were added after the premix was partially polymerized.

Example 19 was prepared in the same way as example 1 except that the premix consisted of 71 parts IOA, 27 parts IBA, and 2 parts AA. In addition, 0.12 parts of 2,4-bis-trichloromethyl-6-(3,4-dimethoxyphenyl)-s-triazine were added after the premix was partially polymerized.

Example 20 was prepared in the same way as example 1 except that the premix consisted of 76 parts IOA, 21 parts IRA, and 3 parts AA. In addition, 0.12 parts of



2,4-bis-trichloromethyl-6-(3,4-dimethoxyphenyl)-s-triazine were added after the premix was partially polymerized.

5 The data of Examples 1-20, as well as comparative examples C1, C2, and C3, are shown in Table II-2. The designation "DNS" means the adhesive did not stick to the substrate. The designation "nt" means not tested.

TABLE II-2

Example	Stainless Steel Peel Strength 24 Hour	10 Second Peel Cold Rolled Steel	1 Min Peel Cold Rolled Steel	RT Shear Minutes	70°C Shear Minutes	Percent Conversion
1	24.1	8.6	14.3	68	nt	>97
2	31.4	6.2	11.8	169	nt	>97
3	52.7	6.7	12.2	381	nt	>97
4	42.4	4.3	11.9	292	nt	>97
5	20.5	2.3	15.5	30	nt	>97
6	27.0	5.8	10.1	214	nt	>97
7	38.2	6.5	11.6	243	nt	>97
8	44.2	4.0	10.4	741	nt	>97
9	37.3	3.7	10.7	185	nt	>97
10	32.3	6.5	12.4	135	nt	>97
11	43.0	5.4	11.6	210	nt	>97
12	42.9	3.8	12.3	758	nt	>97
13	11.5	2.8	10.3	12	nt	>97
14	13.4	5.1	10.8	177	nt	>97
15	20.3	5.2	8.6	186	nt	>97
16	22.5	5.1	7.7	195	nt	>97

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15

17	36.0	4.1	6.0	997	10K+	>97
18	38.7	3.1	6.5	1465	10K+	>97
19	47.7	1.0	4.3	8318	10K+	>97
20	39.1	0.8	2.0	10K+	10K+	>97
C1	51.2	0 (DNS)	0 (DNS)	10K+	nt	>97
C2	37.6	0 (DNS)	0 (DNS)	10K+	nt	>97
C3	61.5	0 (DNS)	0.7	10K+	nt	>97

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III. Tackified Pressure Sensitive Adhesives  
Test Procedures-Tackified Pressure Sensitive Adhesives

Test procedures used in the examples to evaluate tackified pressure sensitive adhesives include the following.

Monomer Conversion Test (Test Procedure A1-III)

The monomer conversion was determined gravimetrically. A sample of the adhesive was weighed after it was coated and subsequently dried at 120°C for 3 hours and then re-weighed. The percent volatiles was taken to be indicative of the monomer conversion.

Monomer Conversion Test (Test Procedure A2-III)

The monomer conversion was determined gravimetrically. 3 in. by 3 in. samples were laminated to a piece of aluminum foil, weighed, and placed in a forced air oven at 250°F for 90 min. Samples were then equilibrated at room temperature and re-weighed for weight loss. The percent volatiles was taken to be indicative of the monomer conversion.

90° Peel Adhesion Test (Test Procedure B1-III)

One-half inch wide strips of a 5 mil adhesive sample were carefully cut and placed onto the substrate of interest. A 5 mil anodized aluminum backing, 0.625 in. wide, was then laminated to the adhesive which is approximately 5 inches long. Test substrates of interest included low energy surfaces such as polypropylene (2" x 5" x 3/16" natural polypropylene panels available from Precision Punch and Plastic, Minneapolis, MN, having a mask on both sides that is removed prior to cleaning and testing) and polycarbonate (Lexan<sup>TM</sup> available from General Electric Co.), and high energy surfaces such as stainless steel (304-2BA 28 gauge stainless steel with a surface roughness of 2.0 ± 1.0 microinches). A free end of the backing to which the adhesive was laminated extended beyond the test substrate so that it could be clamped

to a load cell to determine peel strength. The sample was rolled twice back and forth with a 2 kg hard rubber roller to ensure contact between the adhesive and the test substrate. The adhesive was then removed after a  
5 given dwell time (usually 72 hours unless otherwise noted) at 12"/minute in a 90° peel mode. The peel data are reported in lbs/0.5 in. width. and represent the average of two tests.

The stainless steel substrates were washed once  
10 with acetone and 3 times with a 50/50 isopropanol/water mixture prior to testing. The plastic substrates were washed 3 times with heptane prior to testing.

90° Peel Adhesion Test (Test Procedure B2-III)

One-half inch wide pieces of samples were cut out  
15 and laminated to 5 mil thick anodized aluminum which was 0.625 in. wide. The adhesive thickness was 5 mils. The release liner was then removed from the adhesive and the samples were placed onto either a stainless steel substrate (304 stainless steel with a #7 finish)  
20 or a cold rolled steel substrate (20 gauge cold plate CRS 1018 with mill finish). The stainless steel substrate was cleaned prior to application of adhesive by wiping once with acetone and 3 times with heptane. The cold rolled steel substrate was cleaned prior to  
25 application of adhesive by wiping once with acetone.

Prior to application of the adhesive, an excess of mineral oil was applied to each cold rolled steel substrate with a small piece of cheese cloth and then removed to leave a coating of oil that was  $1.5 \pm 0.25$   
30 mg/in.<sup>2</sup>. A free end of the backing to which the adhesive was laminated extended beyond the test substrate so that it could be clamped to a load cell to determine peel strength. The sample was rolled back and forth twice with a 4.5 lb roller to ensure contact  
35 between the adhesive and the test substrate. The adhesive was then removed after a given dwell time (10

sec., 1 minute, or 24 hours) at 12"/minute in a 90° peel mode.

The values reported are in oz/0.5 in. and represent the average peel values (based on two tests) obtained between 1 and 4 inches on a 5 inch peel sample. All tests were done at room temperature.

Shear Test (Test Procedure C1-III)

A 0.5 inch strip of tape was adhered to a piece of stainless steel (304 stainless steel with a #7 finish) which had been cleaned once with acetone and 3 times with 50/50 isopropanol/water such that a one-half square inch overlap was accomplished. A piece of 5 mil anodized aluminum was then laminated to the entire area of the pressure sensitive adhesive, leaving an additional area to which a load could be applied. The thickness of the adhesive was 5 mils. The sample was then rolled twice back and forth with a 15 pound roller and allowed to dwell for four hours. The 70°C samples were further allowed to dwell for 10 minutes at 70°C. After dwelling the sample was tested at either room temperature or 70°C. At room temperature a 1 kg load was applied to the adhesive and the time before the load fell was recorded. At 70°C a 500g load was applied to the adhesive and the time before the load fell was recorded.

The shear data are reported in minutes and represent the average of two tests.

Shear Test (Test Procedure C2-III)

One-half inch wide pieces of samples were cut out and laminated to 5 mil thick anodized aluminum which was 0.625 in. wide. This construction was placed on stainless steel panels (304 stainless steel with a #7 finish) that had been cleaned by wiping once with acetone and 3 times with heptane. Placement was such that a 1.0 in. x 0.5 in. adhesive sample (adhesive thickness = 5 mils) was in contact with the panel. The

adhesive sample was rolled back and forth twice with a 4.5 lb roller, with some excess material overhanging the sample for attachment of the weight. The samples were then allowed to dwell for 24 hours before the weight was hung on the samples. The 70°C samples were further allowed to dwell for an additional 10 minutes in the oven before the weight was applied. For the room temperature samples, a 1000 g weight was used, whereas for the 70°C samples a 500 g weight was used.

The shear data are reported in minutes until the weight fell and represent the average of two tests.

#### Phase Separation (Test Procedure D-III)

The presence or absence of phase separation was judged by the optical clarity of the resulting polyacrylate/tackifier blend. The visual observation of opacity was taken to be indicative of a phase separation.

#### Examples-Tackified Pressure Sensitive Adhesive

##### Examples 1-56

#### Example 1:

100 parts by weight of iso-octyl acrylate (IOA), iso-bornyl acrylate (IBA), and acrylic acid (AA) with a monomer ratio of 80/19.5/0.5 (IOA/IBA/AA) was blended with 0.04 parts of benzildimethylketal (KB-1, SARTOMER Company) photoinitiator and photopolymerized with an ultraviolet light source under a constant nitrogen purge to a viscosity of about 2000 cps. 0.16 parts of additional benzildimethylketal photoinitiator, 0.15 parts of 2,4-bis(trichloromethyl)-6-(4-methoxyphenyl), and 20 parts of Regalrez 1085 tackifier resin (Hercules Co.) were added to the acrylate syrup and mixed until all of the components had completely dissolved. After mixing, the blend was knife-coated at a 5 mil thickness onto a silicone-treated polyethylene-coated paper release liner. The composite was then exposed to ultraviolet radiation having a spectral output from

300-400 with a maximum at 351 nm in a nitrogen-rich environment. The average intensity was about 2.05 mW/cm<sup>2</sup>. resulting in a total energy of 650 mJ/cm<sup>2</sup>.

Example 2 was prepared in the same way as Example 5 1 except 40 parts of Regalrez 1085 tackifier was used.

Example 3 was prepared in the same way as Example 1 except Regalrez 1094 tackifier (Hercules Co.) was used.

Example 4 was prepared in the same way as Example 10 1 except 40 parts of Regalrez 1094 tackifier was used.

Example 5 was prepared in the same way as Example 1 except Regalrez 1128 tackifier (Hercules Co.) was used.

Example 6 was prepared in the same way as Example 15 1 except 40 parts of Regalrez 1128 tackifier was used.

Example 7 was prepared in the same way as Example 1 except Regalrez 6108 tackifier (Hercules Co.) was used.

Example 8 was prepared in the same way as Example 20 1 except 40 parts of Regalrez 6108 tackifier was used.

Example 9 was prepared in the same way as Example 1 except Regalrez 3102 tackifier (Hercules Co.) was used.

Example 10 was prepared in the same way as Example 25 1 except 40 parts of Regalrez 3102 tackifier was used.

Example 11 was prepared in the same way as Example 1 except Regalrez 5095 tackifier (Hercules Co.) was used.

Example 12 was prepared in the same way as Example 30 1 except 40 parts of Regalrez 5095 tackifier was used.

Example 13 was prepared in the same way as Example 1 except Escorez 5340 tackifier (Exxon Co.) was used.

Example 14 was prepared in the same way as Example 1 except 40 parts of Escorez 5340 tackifier was used.

35 Example 15 was prepared in the same way as Example 1 except Arakawa KE-311 tackifier (Arakawa) was used.



Example 16 was prepared in the same way as Example 1 except 40 parts of Arakawa KE-311 tackifier was used.

Example 17 was prepared in the same way as Example 1 except Escorez 5300 tackifier (Exxon Co.) was used.

5      Example 18 was prepared in the same way as Example 1 except 40 parts of Escorez 5300 tackifier was used.

Example 19 was prepared in the same way as Example 1 except Arkon E90 tackifier (Arakawa) was used.

Example 20 was prepared in the same way as Example 10 1 except 40 parts of Arkon E90 tackifier was used.

Example 21 was prepared in the same way as Example 1 except Arkon P115 tackifier (Arakawa) was used.

Example 22 was prepared in the same way as Example 1 except 40 parts of Arkon P115 tackifier was used.

15      Example 23 was prepared in the same way as Example 1 except Regalite 90 tackifier (Hercules Co.) was used.

Example 24 was prepared in the same way as Example 1 except 40 parts of Regalite 90 tackifier was used.

Example 25 was prepared in the same way as Example 20 1 except Exxon ECR 165B tackifier was used.

Example 26 was prepared in the same way as Example 1 except 40 parts of Exxon ECR 165B tackifier was used.

Example 27 was prepared in the same way as Example 1 except Exxon ECR 177 tackifier was used.

25      Example 28 was prepared in the same way as Example 1 except 40 parts of Exxon ECR 177 tackifier was used.

Example 29 was prepared in the same way as Example 1 except Arkon M100 tackifier (Arakawa) was used.

Example 30 was prepared in the same way as Example 30 1 except 40 parts of Arkon M100 tackifier was used.

Example 31 was prepared in the same way as Example 1 except Arkon M90 tackifier (Arakawa) was used.

Example 32 was prepared in the same way as Example 1 except 40 parts of Arkon M90 tackifier was used.

Example 33 was prepared in the same way as example 1 except Hercotac RT110 tackifier (Hercules Co.) was used.

Example 34 was prepared in the same way as Example 5 1 except 40 parts of Hercotac RT110 tackifier was used.

Example 35 was prepared in the same way as example 1 except Escorez 5380 tackifier (Exxon Co.) was used.

Example 36 was prepared in the same way as Example 1 except 40 parts of Escorez 5380 tackifier was used.

10 Example 37 was prepared in the same way as Example 1 except Foral 85 tackifier (Hercules Co.) was used.

Example 38 was prepared in the same way as Example 1 except 40 parts of Foral 85 tackifier was used.

Example 39 was prepared in the same way as Example 15 1 except Kristalex 5140 tackifier (Hercules Co.) was used.

Example 40 was prepared in the same way as Example 2 except 40 parts of Kristalex 5140 tackifier was used.

Example 41 was prepared in the same way as Example 20 1 except Hercotac 100S tackifier (Hercules Co.) was used.

Example 42 was prepared in the same way as Example 1 except 40 parts of Hercotac 100S tackifier was used.

Example 43 was prepared in the same way as Example 25 1 except Regalite 355 tackifier (Hercules Co.) was used.

Example 44 was prepared in the same way as Example 1 except 40 parts of Regalite 355 tackifier was used.

Example 45 was prepared in the same way as Example 30 1 except Wingtack Plus tackifier (Goodyear Co.) was used.

Example 46 was prepare in the same way as Example 1 except 40 parts of Wingtack Plus tackifier was used.

Example 47 was prepared in the same way as Example 35 1 except Hercotac RT 400 tackifier (Hercules Co.) was used.

Example 48 was prepared in the same way as Example 1 except 40 parts of Hercotac RT 400 tackifier was used.

Example 49 was prepared in the same way as Example 1 except Piccotac HM2162 tackifier (Hercules Co.) was used.

Example 50 was prepared in the same way as Example 1 except 40 parts of Piccotac HM2162 tackifier was used.

Example 51 was prepared in the same way as Example 1 except Kristalex 3100 tackifier (Hercules Co.) was used.

Example 52 was prepared in the same way as Example 1 except 40 parts of Kristalex 3100 tackifier was used.

Example 53 was prepared in the same way as Example 1 except Kristalex 1120 tackifier (Hercules Co.) was used.

Example 54 was prepared in the same way as Example 1 except 40 parts of Kristalex 1120 tackifier was used.

Example 55 was prepared in the same way as Example 1 except Piccolyte A135 tackifier (Hercules Co.) was used.

Example 56 was prepared in the same way as Example 1 except 40 parts of Piccolyte A135 tackifier was used.

The inhibition factor and phase separation characteristics of the above examples are shown in Table III-2. The polypropylene peel strength of several samples were determined according to Test Procedure B1-III and are reported in Table III-2 as well. If the samples possessed an inhibition factor greater than 1.0 the sample was dried in a 120°C oven to reduce the inhibition factor below 1 prior to testing. The designation "nt" means not tested. The designation "na" means not applicable. The designation "nc" means not conclusive.

TABLE III-2

Example	Inhibition Factor	Phase separation	Polypropylene peel strength (lb/0.5")
5	1	no	nt
	2	no	nt
	3	no	nt
	4	yes	3.37
	5	yes	3.20
10	6	yes	2.71
	7	no	2.48
	8	no	1.52
	9	no	2.78
	10	no	1.07
15	11	no	nt
	12	no	nt
	13	yes	nt
	14	yes	nt
	15	no	2.53
20	16	no	3.90
	12	yes	nt
	18	yes	nt
	19	no	4.29
	20	no	1.90
25	21	yes	3.01
	22	no	3.60
	23	no	nt
	24	no	nt
	25	yes	nt
30	24	Yes	nt
	27	yes	nt
	28	yes	nt
	29	no	2.93

5	30	1.89	no	3.90
	31	0.96	no	2.72
	32	1.88	no	4.04
	33	1.25	no	1.26
	34	3.11	yes	0.79
10	35	1.34	yes	nt
	36	2.42	yes	nt
	37	1.52	no	nt
	38	2.83	no	nt
	39	1.61	nc	nt
15	40	2.71	nc	0.69
	41	1.66	no	2.29
	42	4.58	no	2.10
	43	2.25	no	5.14
	44	2.99	no	2.94
20	45	2.34	no	3.06
	46	5.74	no	5.33
	47	2.68	no	2.90
	48	5.95	no	0.72
	49	2.94	no	2.82
25	50	6.50	no	3.98
	51	3.03	nc	nt
	52	4.11	nc	0.55
	53	>6.5	na	nt
	54	>6.5	na	nt
	55	>6.5	na	nt
	56	>6.5	na	nt

30        The data of Table III-2 shows that several commercial tackifiers are soluble in the non-polar acrylate pressure sensitive adhesive matrix but that only the Regalrez tackifying resins have low inhibition factors as well.

Examples 57-115

Example 57 was prepared in the same way as Example 1 except an 85/15/0 IOA/IBA/AA monomer ratio was used.

Example 58 was prepared in the same way as Example 57 except 40 parts of Regalrez 1085 tackifier was used.

Example 59 was prepared in the same way as Example 1 except an 85/14/1 IOA/IBA/AA monomer ratio was used.

Example 60 was prepared in the same way as Example 1 except an 85/13/2 IOA/IBA/AA monomer ratio was used.

10 Example 61 was prepared in the same way as Example 1 except an 85/11/4 IOA/IBA/AA monomer ratio was used.

Example 62 was prepared in the same way as Example 57 except 20 parts of Regalrez 6108 tackifier was used.

Example 63 was prepared in the same way as Example 15 62 except 40 parts of Regalrez 6108 tackifier was used.

Example 64 was prepared in the same way as Example 62 except an IOA/IBA/AA ratio of 85/14/1 was used.

Example 65 was prepared in the same way as Example 64 except 40 parts of Regalrez 6108 tackifier was used.

20 Example 66 was prepared in the same way as Example 64 except an IOA/IBA/AA ratio of 85/13/2 was used.

Example 67 was prepared in the same way as Example 66 except an IOA/IBA/AA ratio of 85/12/3 was used.

Example 68 was prepared in the same way as Example 25 57 except 20 parts of Regalrez 3102 tackifier was used.

Example 69 was prepared in the same way as Example 68 except 40 parts of Regalrez 3102 tackifier was used.

Example 70 was prepared in the same way as Example 68 except an IOA/IBA/AA ratio of 85/14/1 was used.

30 Example 71 was prepared in the same way as Example 70 except 40 parts of Regalrez 3102 tackifier was used.

Example 72 was prepared in the same way as Example 70 except an IOA/IBA/AA ratio of 85/13/2 was used.

Example 73 was prepared in the same way as Example 35 72 except an IOA/IBA/AA ratio of 85/12/3 was used.

Example 74 was prepared in the same way as Example 57 except 20 parts of Regalrez 1094 tackifier was used.

Example 75 was prepared in the same way as Example 74 except 40 parts of Regalrez 1094 tackifier was used.

5 Example 76 was prepared in the same way as Example 74 except an IOA/IBA/AA ratio of 85/14/1 was used.

Example 77 was prepared in the same way as Example 74 except an IOA/IBA/AA ratio of 85/13/2 was used.

Example 78 was prepared in the same way as Example 10 57 except an IOA/IBA/AA ratio of 90/9/1 was used.

Example 79 was prepared in the same way as Example 78 except an IOA/IBA/AA ratio of 81/13/1 was used.

Example 80 was prepared in the same way as Example 79 except 30 parts of Regalrez 1085 was used.

15 Example 81 was prepared in the same way as Example 79 except an IOA/IBA/AA ratio of 76/23/1 was used.

Example 82 was prepared in the same way as Example 81 except 40 parts of Regalrez 1085 was used.

Example 83 was prepared in the same way as Example 20 81 except an IOA/IBA/AA ratio of 81/17/2 was used.

Example 84 was prepared in the same way as Example 81 except an IOA/IBA/AA ratio of 76/22/2 was used.

Example 85 was prepared in the same way as Example 62 except an IOA/IBA/AA ratio of 90/9/1 was used.

25 Example 86 was prepared in the same way as Example 85 except 30 parts of Regalrez 6108 was used.

Example 87 was prepared in the same way as Example 85 except an IOA/IBA/AA ratio of 81/18/1 was used.

Example 88 was prepared in the same way as Example 30 87 except 40 parts of Regalrez 5108 was used.

Example 89 was prepared in the same way as Example 85 except an IOA/IBA/AA ratio of 76/23/1 was used.

Example 90 was prepared in the same way as Example 89 except 40 parts of Regalrez 5108 was used.

35 Example 91 was prepared in the same way as Example 85 except an IOA/IBA/AA ratio of 90/8/2 was used.

Example 92 was prepared in the same way as Example 91 except an IOA/IBA/AA ratio of 85/13/2 was used.

Example 93 was prepared in the same way as Example 92 except an IOA/IBA/AA ratio of 81/17/2 was used.

5       Example 94 was prepared in the same way as Example 93 except 30 parts of Regalrez 6108 was used.

Example 95 was prepared in the same way as Example 94 except 40 parts of Regalrez 6108 was used.

10       Example 96 was prepared in the same way as Example 92 except an IOA/IBA/AA ratio of 76/22/2 was used.

Example 97 was prepared in the same way as Example 96 except 30 parts of Regalrez 6108 was used.

Example 98 was prepared in the same way as Example 97 except 40 parts of Regalrez 6108 was used.

15       Example 99 was prepared in the same way as Example 68 except an IOA/IBA/AA ratio of 90/9/1 was used.

Example 100 was prepared in the same way as Example 99 except 30 parts of Regalrez 3102 was used.

20       Example 101 was prepared in the same way as Example 68 except an IOA/IBA/AA ratio of 81/18/1 was used.

Example 102 was prepared in the same way as Example 101 except 30 parts of Regalrez 3102 was used.

25       Example 103 was prepared in the same way as Example 68 except an IOA/IBA/AA ratio of 76/23/1 was used.

Example 104 was prepared in the same way as Example 103 except 30 parts of Regalrez 3102 was used.

30       Example 105 was prepared in the same way as Example 68 except an IOA/IBA/AA ratio of 90/8/2 was used.

Example 106 was prepared in the same way as Example 68 except an IOA/IBA/AA ratio of 81/17/2 was used.

35       Example 107 was prepared in the same way as Example 106 except 40 parts of Regalrez 3102 was used.



Example 108 was prepared in the same way as Example 68 except an IOA/IBA/AA ratio of 76/22/2 was used.

Example 109 was prepared in the same way as  
5 Example 74 except 10 parts of Regalrez 1094 was used and a monomer ratio of 90/9/1 IOA/IBA/AA was used.

Example 110 was prepared in the same way as Example 74 except a monomer ratio of 81/18/1 IOA/IBA/AA was used.

10 Example 111 was prepared in the same way as Example 109 except a monomer ratio of 76/23/1 IOA/IBA/AA was used.

Example 112 was prepared in the same way as Example 111 except 20 parts of Regalrez 1094 was used.

15 Example 113 was prepared in the same way as Example 109 except 10 parts of Regalrez 3102 was used, 0.09 parts of 2,4-bis(trichloromethyl)-6-(4-methoxyphenyl)-s-triazine crosslinker was used, N-octyl acrylamide (NOA) was used instead of IBA, and the  
20 monomer ratio was 89/10.5/0.5 IOA/NOA/AA.

Example 114 was prepared in the same way as Example 113 except that 30 parts Regalrez 3102 was used.

Example 115 was prepared in the same way as  
25 Example 62 except an IOA/IBA/AA ratio of 95/4.75/0.25 was used and 25 parts Regalrez 6108 was used.

#### Comparative Example C1

90 parts by weight of iso-octyl acrylate (IOA) and 10 parts acrylic acid (AA) were blended with 0.04 parts  
30 of 2,2-dimethoxy-2-phenylacetophenone photoinitiator (Irgacure<sup>TM</sup> 651, available from Ciba-Geigy Corp.) and photopolymerized with an ultraviolet light source under a constant nitrogen purge to a viscosity of about 3000 cps. 0.16 parts of additional 2,2-dimethoxy-2-  
35 phenylacetophenone photoinitiator and 0.15 parts of 2,4-bis(trichloromethyl)-6-(4-methoxyphenyl)-s-triazine

were added to the acrylate syrup and mixed until all of the components had completely dissolved. After mixing the blend was knife-coated at a 5 mil thickness onto a silicone-treated polyethylene-coated paper release  
 5 liner. The composite was then exposed to ultraviolet radiation having a spectral output from 300-400 with a maximum at 351 nm in a nitrogen-rich environment. An intensity of about 1.0 mW/cm<sup>2</sup> was used for the first one-third of the exposure time and an intensity of  
 10 about 2.2 mW/cm<sup>2</sup> was used for the second two-thirds of the exposure time, resulting in a total energy of 250 mJ/cm<sup>2</sup>.

Comparative example C2 was prepared in the same way as comparative example C1 except a premix of 94  
 15 parts IOA and 6 parts AA was used.

Comparative example C3 was prepared in the same way as comparative example C1 except a premix of 100 parts IOA and 0 parts AA was used.

The data of Example 57-115 and comparative  
 20 examples C1, C2, and C3 are shown in Table III-3. Test procedures A1-III, B1-III, and C1-III were used to generate the data. The designation "nt" means not tested.

25

TABLE III-3

Ex.	St.St. Peel (lb/0.5")	Poly- propylene peel (lb/0.5")	Room Temp Shear	70°C Shear	Percent Con- version
57	3.83	3.63	313	35	>98.5%
58	3.73	3.87	1006	6	>98.5%
59	4.15	4.05	5867	10K+	>98.5%
30 60	2.66	2.84	7222	10K+	>98.5%
61	2.71	2.75	10K+	859	>98.5%
62	3.15	3.64	535	34	>98.5%
63	4.03	6.24	719	23	>98.5%

5	64	4.22	3.54	7223	10K+	>98.5%
	65	5.33	6.84	2916	41	>98.5%
	66	6.92	3.85	10K+	10K+	>98.5%
	67	4.04	3.30	10K+	10K+	>98.5%
	68	3.21	2.52	880	30	>98.5%
10	69	4.24	2.57	632	5	>98.5%
	70	4.11	2.67	4900	10K+	>98.5%
	71	4.94	3.04	1338	12	>98.5%
	72	3.62	2.58	10K+	10K+	>98.5%
	73	4.27	3.63	10K+	10K+	>98.5%
15	74	2.58	3.24	708	nt	>98.5%
	75	3.22	3.26	1301	nt	>98.5%
	76	3.50	3.54	10K+	10K+	>98.5%
	77	3.90	3.38	10K+	10K+	>98.5%
	78	2.69	3.55	2003	1870	>98.5%
20	79	3.24	3.57	10K+	3961	>98.5%
	80	2.57	2.47	1865	27	>98.5%
	81	4.32	3.34	4639	1714	>98.5%
	82	3.00	3.91	242	5	>98.5%
	83	3.05	3.00	5021	1902	>98.5%
25	84	3.39	3.56	3040	888	>98.5%
	85	3.28	2.82	10K+	10K+	>98.5%
	86	3.36	4.87	10K+	5307	>98.5%
	87	4.96	3.01	10K+	10K+	>98.5%
	88	5.60	5.65	2094	22	>98.5%
30	89	3.76	3.43	10K+	1376	>98.5%
	90	4.76	3.10	5605	18	>98.5%
	91	3.34	2.87	10K+	10K+	>98.5%
	92	6.92	3.85	10K+	10K+	>98.5%
	93	4.86	3.35	10K+	10K+	>98.5%
	94	4.20	4.61	10K+	1287	>98.5%
	95	5.73	3.18	10K+	60	>98.5%

5	96	4.55	1.75	10K+	10K+	>98.5%
	97	5.88	5.44	10K+	207	>98.5%
	98	4.58	4.38	7187	26	>98.5%
	99	3.08	2.29	10K+	10K+	>98.5%
	100	4.55	2.43	4516	1795	>98.5%
10	101	4.64	3.22	5396	10K+	>98.5%
	102	4.68	1.63	2513	13	>98.5%
	103	3.81	3.00	6798	10K+	>98.5%
	104	4.89	1.64	10K+	155	>98.5%
	105	3.72	2.41	10K+	10K+	>98.5%
15	106	3.61	1.96	10K+	10K+	>98.5%
	107	6.63	4.62	4906	49	>98.5%
	108	4.46	4.11	10K+	10K+	>98.5%
	109	2.38	2.85	223	10K+	>98.5%
	110	3.06	3.90	10K+	10K+	>98.5%
20	111	2.68	3.05	10K+	10K+	>98.5%
	112	4.58	4.54	10K+	10K+	>98.5%
	113	2.65	2.46	2297	150	>98.5%
	114	3.66	4.06	616	12	>98.5%
	115	nt	nt	2504	329	>98.5%
25	C1	5.33	0.43	10,000+	10,000+	>98.5%
	C2	3.73	1.29	10,000+	10,000+	>98.5%
	C3	1.35	1.53	2	3	>98.5%

#### Examples 116-124

##### **EXAMPLE 116**

83 parts IOA and 17 parts IBA were mixed together in a jar under a constant nitrogen purge along with 0.04 parts of Irgacure 651 photoinitiator from Ciba-Geigy Corp. (2,2-dimethoxy-2-phenylacetophenone). This mixture was exposed to a low intensity ultraviolet light under a constant nitrogen purge while stirring until a coatable viscosity syrup was obtained. The

conversion of this syrup was between 4 and 10% and the viscosity was about 3,000 cps. 0.12 parts of 2,4-bis(trichloromethyl)-6-(3,4-dimethoxyphenyl)-s-triazine and an additional 0.16 parts Irgacure 651 were then  
5 added to the prepolymerized syrup, along with 20.5 parts of Regalrez 6108 tackifier (Hercules Co.). The ingredients were mixed thoroughly until homogeneous and then knife-coated at a 5 mil thickness onto a silicone-treated polyethylene-coated paper release liner. The  
10 composite was then exposed to ultraviolet radiation having a spectral output from 300-400 with a maximum at 351 nm in a nitrogen-rich environment. The average intensity was about 2.05 mW/cm<sup>2</sup>. resulting in a total energy of 650 mJ/cm<sup>2</sup>.

15 Example 117 was prepared in the same way as example 116 except that the monomer mixture was 77 parts IOA and 23 parts IBA. Also, 13.6 parts Regalrez 6108 was used.

Example 118 was prepared in the same way as  
20 example 116 except that the monomer mixture was 71 parts IOA and 21 parts IBA. Also, 7.5 parts Regalrez 6108 was used.

Example 119 was prepared in the same way as example 116 except that the monomer mixture was 84  
25 parts IOA, 15 parts IBA, and 1 part AA. Also, 20.5 parts Regalrez 6108 was used.

Example 120 was prepared in the same way as example 116 except that the monomer mixture was 81 parts IOA, 18 parts IBA, and 1 part AA. Also, 17.6  
30 parts Regalrez 6108 was used.

Example 121 was prepared in the same way as example 116 except that the monomer mixture was 72 parts IOA, 27 parts IBA, and 1 part AA. Also, 7.5 parts Regalrez 6108 was used.

35 Example 122 was prepared in the same way as example 116 except that the monomer mixture was 83

parts IOA and 17 parts IBA. Also, 5 parts Regalrez 6108 was used.

Example 123 was prepared in the same way as example 122 except that 15 parts Regalrez 6108 was used.

Example 124 was prepared in the same way as example 122 except that 30 parts Regalrez 6108 was used.

#### Comparative Example C4

94 parts IOA and 6 parts AA were mixed together in a jar under a constant nitrogen purge along with 0.04 parts of Irgacure 651 photoinitiator from Ciba-Geigy Corp. (2,2-dimethoxy-2-phenylacetophenone). This mixture was partially polymerized under a nitrogen-rich atmosphere to provide a coatable syrup having a viscosity of about 3,000 cps. 0.16 parts of 2,4-bis(trichloromethyl)-6-(3,4-dimethoxyphenyl)-s-triazine and an additional 0.16 parts Irgacure 651 were then added to the prepolymerized syrup and it was then knife-coated onto a release coated paper backing at a thickness of 5 mils. The resulting coating was then exposed to ultraviolet radiation having a spectral output from 300-400 with a maximum at 351 nm in a nitrogen-rich environment. The average intensity was about 2.05 mW/cm<sup>2</sup>. resulting in a total energy of 650 mJ/cm<sup>2</sup>.

Comparative example C5 was prepared in the same way as comparative example C4 except that a premix of 10 parts AA and 90 parts IOA was used. In addition, 0.12 parts triazine was used. Comparative example C6 was prepared in the same way as comparative example C4 except that a premix of 14 parts AA and 86 parts IOA was used.

Peel and shear data for examples 116-124 and comparative examples C4, C5, and C6 are set forth in

Table III-4. The data was generated according to Test Procedures A2-III, B2-III, and C2-III.

TABLE III-4  
PATENT EXAMPLES FOR TACKIFIED NPAS FOR OILY METAL SURFACES

Example	Stainless Steel Peel 24 Hour	Room Temp Shear	70°C Shear	10 Second Peel Cold Rolled Steel	1 Min. Peel Cold Rolled Steel	Percent Conversion
116	32.6	1020	85	4.0	5.1	>98
117	41.9	581	300	4.7	6.7	>98
118	40.9	481	331	4.0	4.7	>98
119	61.1	1927	426	4.6	10.3	>98
120	50.7	5391	338	5.4	9.2	>98
121	47.0	10K+	10K+	4.4	8.8	>98
122	36.6	127	599	7.3	10.5	>98
123	43.5	1314	10K+	9.3	12.4	>98
124	56.8	810	17	7.9	12.5	>98
C4	51.2	O(DNS)	O(DNS)	10K+	nt	>97
C5	37.6	O(DNS)	O(DNS)	10K+	nt	>97
C6	61.5	O(DNS)	0.7	10K+	nt	>97

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Other embodiments are within the following claims.

What is claimed is:

1. A pressure sensitive adhesive comprising the reaction product of starting materials comprising:

5 (a) 25-97 parts by weight of an acrylic acid ester of a monohydric alcohol whose homopolymer has a  $T_g$  less than  $0^\circ\text{C}$ ;

(b) 3-75 parts by weight of a non-polar ethylenically unsaturated monomer whose homopolymer has a solubility  
10 parameter of no greater than 10.50 and a  $T_g$  greater than  $15^\circ\text{C}$ ; and

(c) 0-5 parts by weight of a polar ethylenically unsaturated monomer whose homopolymer has a solubility parameter of greater than 10.50 and a  $T_g$  greater than  $15^\circ\text{C}$ ,  
15 the relative amounts of said acrylic acid ester, said non-polar ethylenically unsaturated monomer, and said polar ethylenically unsaturated monomer being chosen such that the  $90^\circ$  peel adhesion of said reaction product to a polypropylene surface is at least 2 lbs/0.5 in. after a 72  
20 hour dwell at room temperature as measured according to Test Procedure B-I.

2. A pressure sensitive adhesive comprising the reaction product of starting materials comprising:

(a) 25-97 parts by weight of an acrylic acid ester of  
25 a monohydric alcohol whose homopolymer has a  $T_g$  less than  $0^\circ\text{C}$ ;

(b) 3-75 parts by weight of a non-polar ethylenically unsaturated monomer whose homopolymer has a solubility parameter of no greater than 10.50 and a  $T_g$  greater than  
30  $15^\circ\text{C}$ ; and

(c) 0-5 parts by weight of a polar ethylenically unsaturated monomer whose homopolymer has a solubility parameter of greater than 10.50 and a  $T_g$  greater than  $15^\circ\text{C}$ ,  
the relative amounts of said acrylic acid ester, said  
35 non-polar ethylenically unsaturated monomer, and said polar ethylenically unsaturated monomer being chosen such that

the 90° peel adhesion of said reaction product to a surface provided with  $1.5 \pm 0.25$  mg/in<sup>2</sup> oil is greater than zero after a 10 second dwell at room temperature as measured according to Test Procedure B-II.

- 5        3. A pressure sensitive adhesive comprising  
         (a) the reaction product of starting materials comprising:  
             (i) 25-98 parts by weight of an acrylic acid ester of  
             a monohydric alcohol whose homopolymer has a  $T_g$  less than  
10    0°C;  
             (ii) 2-75 parts by weight of a non-polar ethylenically  
             unsaturated monomer, other than a methacrylate monomer,  
             whose homopolymer has a solubility parameter of no greater  
             than 10.50 and a  $T_g$  greater than 15°C; and  
15        (iii) 0-5 parts by weight of a polar ethylenically  
             unsaturated monomer whose homopolymer has a solubility  
             parameter of greater than 10.50 and a  $T_g$  greater than 15°C;  
             and  
             (b) at least one tackifier that is miscible in said  
20    reaction product at room temperature, with the proviso that  
         the pressure sensitive adhesive contains essentially no  
         emulsifier.

         4. The pressure sensitive adhesive of claim 1,  
         wherein the relative amounts of said acrylic acid ester,  
25    said non-polar ethylenically unsaturated monomer, and said  
         polar ethylenically unsaturated monomer are chosen such  
         that the 90° peel adhesion of said reaction product to a  
         polypropylene surface is at least 3 lbs/0.5 in. after a 72  
         hour dwell at room temperature as measured according to  
30    Test Procedure B-I.

         5. The pressure sensitive adhesive of claim 2,  
         wherein the relative amounts of said acrylic acid ester,  
         said non-polar ethylenically unsaturated monomer, and said  
         polar ethylenically unsaturated monomer are chosen such  
35    that the 90° peel adhesion of said reaction product to a  
         surface provided with  $1.5 \pm 0.25$  mg/in<sup>2</sup> oil is at least 2  
         oz/0.5 in. after a 10 second dwell at room temperature as  
         measured according to Test Procedure B-II.

6. The pressure sensitive adhesive of claim 2,  
wherein the relative amounts of said acrylic acid ester,  
said non-polar ethylenically unsaturated monomer, and said  
polar ethylenically unsaturated monomer are chosen such  
5 that the 90° peel adhesion of said reaction product to a  
surface provided with  $1.5 \pm 0.25$  mg/in<sup>2</sup> oil is at least 5  
oz/0.5 in. after a 1 minute dwell at room temperature as  
measured according to Test Procedure B-II.

7. The pressure sensitive adhesive of claim 3,  
10 wherein the relative amounts of said acrylic acid ester,  
said non-polar ethylenically unsaturated monomer, and said  
polar ethylenically unsaturated monomer are chosen such  
that the 90° peel adhesion of said adhesive to a  
polypropylene surface is at least 2 lbs/0.5 in. after a 72  
15 hour dwell at room temperature as measured according to  
Test Procedure B1-III.

8. The pressure sensitive adhesive of claim 3,  
wherein the relative amounts of said acrylic acid ester,  
said non-polar ethylenically unsaturated monomer, and said  
20 polar ethylenically unsaturated monomer are chosen such  
that the 90° peel adhesion of said adhesive to a  
polypropylene surface is at least 5 lbs/0.5 in. after a 72  
hour dwell at room temperature as measured according to  
Test Procedure B1-III.

25 9. The pressure sensitive adhesive of claim 3,  
wherein the relative amounts of said acrylic acid ester,  
said non-polar ethylenically unsaturated monomer, and said  
polar ethylenically unsaturated monomer are chosen such  
that the 90° peel adhesion of said adhesive to a surface  
30 provided with  $1.5 \pm 0.25$  mg/in<sup>2</sup> oil is greater than zero after  
a 10 second dwell at room temperature as measured according  
to Test Procedure B2-III.

10. The pressure sensitive adhesive of claim 3,  
wherein the relative amounts of said acrylic acid ester,  
35 said non-polar ethylenically unsaturated monomer, and said  
polar ethylenically unsaturated monomer are chosen such  
that the 90° peel adhesion of said adhesive to a surface  
provided with  $1.5 \pm 0.25$  mg/in<sup>2</sup> oil is at least 2 oz/0.5 in.

after a 10 second dwell at room temperature as measured according to Test Procedure B2-III.

11. The pressure sensitive adhesive of claim 3, wherein the relative amounts of said acrylic acid ester, said non-polar ethylenically unsaturated monomer, and said polar ethylenically unsaturated monomer are chosen such that the 90° peel adhesion of said adhesive to a surface provided with  $1.5 \pm 0.25$  mg/in<sup>2</sup> oil is at least 5 oz/0.5 in. after a 1 minute dwell at room temperature as measured according to Test Procedure B2-III.

12. The pressure sensitive adhesive of one of claims 1 to 3, comprising 40-85 parts by weight of said acrylic acid ester.

13. The pressure sensitive adhesive of one of claims 1 to 3, comprising 15-60 parts by weight of said non-polar ethylenically unsaturated monomer.

14. The pressure sensitive adhesive of one of claims 1 to 3, comprising an acrylic acid ester selected from the group consisting of isooctyl acrylate, 2-ethyl hexyl acrylate, isononyl acrylate, isodecyl acrylate, decyl acrylate, lauryl acrylate, hexyl acrylate, butyl acrylate, octadecyl acrylate, and combinations thereof.

15. The pressure sensitive adhesive of one of claims 1 to 3, comprising a non-polar ethylenically unsaturated monomer other than a methacrylate monomer.

16. The pressure sensitive adhesive of one of claims 1 to 3, comprising a non-polar ethylenically unsaturated monomer selected from the group consisting of 3,3,5 trimethylcyclohexyl acrylate, cyclohexyl acrylate, isobornyl acrylate, N-octyl acrylamide, t-butyl acrylate, and combinations thereof.

17. The pressure sensitive adhesive of one of claims 1 to 3, comprising a polar ethylenically unsaturated monomer selected from the group consisting of acrylic acid, itaconic acid, N,N dimethylacrylamide, N-vinyl-2-pyrrolidone, N-vinyl caprolactam, acrylonitrile, tetrahydrofurfuryl acrylate, glycidyl acrylate, 2-

phenoxyethylacrylate, benzylacrylate, and combinations thereof.

18. The pressure sensitive adhesive of one of claims 1 to 3, wherein said non-polar ethylenically unsaturated monomer is isobornyl acrylate.

19. The pressure sensitive adhesive of one of claims 1 to 3, comprising the reaction product of isooctyl acrylate, isobornyl acrylate, and acrylic acid.

20. The pressure sensitive adhesive of one of claims 1 to 3, comprising the reaction product of isooctyl acrylate and isobornyl acrylate.

21. An adhesive consisting essentially of:

(A) the reaction product of:

(i) 25-97 parts by weight of an acrylic acid ester of a monohydric alcohol whose homopolymer has a  $T_g$  less than  $0^\circ\text{C}$ ;

(ii) 3-75 parts by weight of a non-polar ethylenically unsaturated monomer other than a methacrylate monomer whose homopolymer has a solubility parameter of no greater than 10.50 and a  $T_g$  greater than  $15^\circ\text{C}$ ;

(iii) 0-5 parts by weight of a polar ethylenically unsaturated monomer whose homopolymer has a solubility parameter of greater than 10.50 and a  $T_g$  greater than  $15^\circ\text{C}$ ; and, optionally,

(iv) a crosslinking agent; and, optionally,

(B) one or more additives selected from the group consisting essentially of microspheres, plasticizers, tackifiers, coloring agents, reinforcing agents, fire retardants, foaming agents, thermally conductive agents, electrically conductive agents, post-curing agents, accelerators, and combinations thereof.

## INTERNATIONAL SEARCH REPORT

Inter national Application No

PCT/US 94/12993

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 6 C09J133/00 C08F220/18

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09J C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,93 15333 (MINNESOTA MINING AND MANUFACTURING COMPANY) 5 August 1993  see page 30, line 9 - line 13; examples 1,2  ---	1,2,4-6, 12-16, 18,20,21
X	US,A,3 491 070 (DAVID E. WEAVER) 20 January 1970  ---	1,2,4-6, 12-16
A	EP,A,0 546 746 (MINNESOTA MINING AND MANUFACTURING COMPANY) 16 June 1993 see claims; example 2  ---	1
A	EP,A,0 303 430 (MINNESOTA MINING AND MANUFACTURING COMPANY) 15 February 1989 see claims; table XII  ---  -/--	1,3

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

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Date of the actual completion of the international search

15 March 1995

Date of mailing of the international search report

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# INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WO,A,81 02262 (MINNESOTA MINING AND MANUFACTURING COMPANY) 20 August 1981 see page 7, line 16 - line 20; claims; examples 14-16</p> <p>-----</p>	1,3



# INTERNATIONAL SEARCH REPORT

information on patent family members

Inter. nal Application No

PCT/US 94/12993

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9315333	05-08-93	US-A- 5262232	16-11-93
		AU-B- 3336593	01-09-93
		CA-A- 2128515	05-08-93
		EP-A- 0621931	02-11-94
US-A-3491070	20-01-70	BE-A- 707069	01-04-68
		CH-A- 481199	15-11-69
		DE-A- 1719132	12-08-71
		FR-A- 1545218	
		GB-A- 1202379	19-08-70
		LU-A- 54953	16-02-68
		NL-A- 6715900	27-05-68
EP-A-0546746	16-06-93	AU-A- 2976492	10-06-93
		CA-A- 2083625	10-06-93
		JP-A- 5271314	19-10-93
EP-A-0303430	15-02-89	DE-D- 3886470	03-02-94
		DE-T- 3886470	14-07-94
		ES-T- 2048202	16-03-94
		JP-A- 1066280	13-03-89
		US-A- 5028484	02-07-91
WO-A-8102262	20-08-81	US-A- 4330590	18-05-82
		AU-B- 541219	20-12-84
		AU-A- 6922781	31-08-81
		CA-A- 1157998	29-11-83
		DE-A- 3105343	10-12-81
		EP-A,B 0045802	17-02-82
		US-A- 4391687	05-07-83

